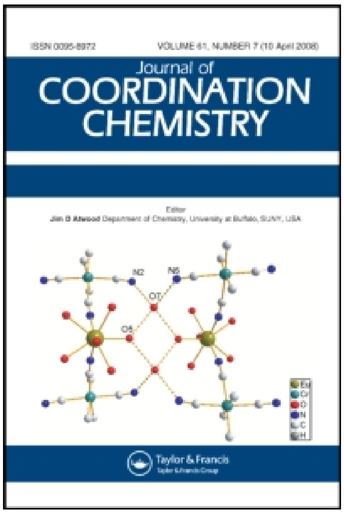


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

PROTONATED LIGAND OUTER-SPHERE COMPLEXES FORMED FROM THE REACTION OF $SnCl_4$ WITH BENZALIDENEANILINE AND RELATED IMINES: X-RAY CRYSTAL STRUCTURE OF BIS[*N*-BENZALIDENEANILINIUM] HEXACHLOROSTANNATE(IV)

Siang-Guan Teoh[a]; Guan-Yeow Yeap[a]; Soon-Beng Teo[a]; Jean-Paul Declercq[b]
[a] School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia [b] Laboratoire de Chimie Physique et de Cristallographie, Universite Catholique de Louvain, Louvain-la-Neuve, Belgium

To cite this Article Teoh, Siang-Guan , Yeap, Guan-Yeow , Teo, Soon-Beng and Declercq, Jean-Paul(1995) 'PROTONATED LIGAND OUTER-SPHERE COMPLEXES FORMED FROM THE REACTION OF $SnCl_4$ WITH BENZALIDENEANILINE AND RELATED IMINES: X-RAY CRYSTAL STRUCTURE OF BIS[*N*-BENZALIDENEANILINIUM] HEXACHLOROSTANNATE(IV)', Journal of Coordination Chemistry, 36: 3, 215 — 223

To link to this Article: DOI: 10.1080/00958979508022563

URL: http://dx.doi.org/10.1080/00958979508022563

J. Coord. Chem., 1995, Vol 36, pp. 215–223
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published under license by
Gordon and Breach Science Publishers SA
Printed in Malaysia

PROTONATED LIGAND OUTER-SPHERE COMPLEXES FORMED FROM THE REACTION OF $SnCl_4$ WITH BENZALIDENEANILINE AND RELATED IMINES: X-RAY CRYSTAL STRUCTURE OF BIS[*N*-BENZALIDENEANILINIUM] HEXACHLOROSTANNATE(IV)

SIANG-GUAN TEOH,* GUAN-YEOW YEAP, SOON-BENG TEO

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

and JEAN-PAUL DECLERCQ

Laboratoire de Chimie Physique et de Cristallographie, Universite Catholique de Louvain,
Place L. Pasteur 1, B-1348, Louvain-la-Neuve, Belgium

(Received March 23, 1995)

The reaction of tin(IV) chloride with the Schiff base *N*-benzalideneaniline in ethanol and dichloromethane (1:1), results in the formation of the bis[*N*-benzalideneanilinium] hexachlorostannate(IV). The protonation of *N*-benzalidineaniline at the imine nitrogen and the conversion of $SnCl_4$ to $[SnCl_6]^{2-}$ via halide addition occurs without the addition of any external pH agent. The unipositive protonated ligands form an outer-sphere complex with the hexachlorostannate dianion *via* hydrogen bonds between the chlorine and imino nitrogen atoms. A benzaldehye molecule is present in the crystal lattice in the $[(BENZH)^+]_2[SnCl_6]^{2-}$ to benzaldehyde (C_6H_5CHO) ratio of 1:1

KEYWORDS: bis[*N*-benzalideneanilinium] hexachlorostannate(IV), tin(IV) chloride complex salt, X-ray analysis

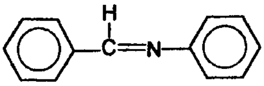
INTRODUCTION

The reactions of inorganic tin(IV) and organotin(IV) compounds with aromatic Schiff bases containing 2-OH substituent in the aldehyde fragment, usually lead to the formation of adducts whereby monodentate coordination *via* the phenolic oxygen atom occurs.[1–6] However, our recent studies show that reactions of tin compounds with Schiff bases having 4-OH or 2-OCH_3 substituents lead to complex salt formation in which the central tin-containing ions $[Ph_2SnCl_4]^{2-}$ and $[Me_2SnCl_3]^-$ are counteracted by the corresponding protonated *N*-(4-hydroxybenzalidene)-4-methoxyaniline[7] and *N*-(2-methoxynaphthalidene)-3-methoxyaniline[8] ions, respectively. In this paper,

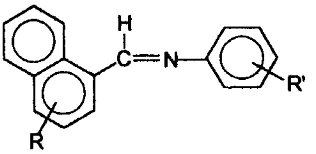
---

* Author for correspondence.

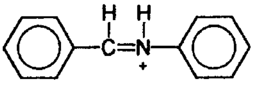
we report reactions of $SnCl_4$ with the Schiff bases **1a-4a** which lead to the formation of complex salts containing the corresponding protonated ligands (**1b-4b**). The complex salt $[(BENZH)^+]_2[SnCl_6]^{2-}[C_6H_5CHO]$ derived from the reaction of $SnCl_4$ with BENZ has been characterized by X-ray analysis and the results are reported along with microanalytical, IR, ^1H and ^{13}C NMR spectroscopic data for the various compounds obtained.



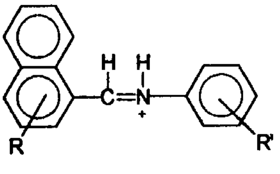
Ligand	Abbreviation
1a	BENZ



Ligand	R	R'	Abbreviation
2a	2-OCH_3	2-OCH_3	2MeONAP-2MeO
3a	2-OCH_3	3-OCH_3	2MeONAP-3MeO
4a	4-OCH_3	2-OCH_3	4MeONAP-2MeO



Protonated ligand	Abbreviation
1b	$(BENZH)^+$



Protonated ligand	R	R'	Abbreviation
2b	2-OCH_3	2-OCH_3	$(2MeONAPH\text{-}2MeO)^+$
3b	2-OCH_3	3-OCH_3	$(2MeONAPH\text{-}3MeO)^+$
4b	4-OCH_3	2-OCH_3	$(4MeONAPH\text{-}2MeO)^+$

EXPERIMENTAL

General and instrumental

Carbon, hydrogen and nitrogen analyses were carried out at the School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia. Tin was estimated using an Instrumentation Laboratory model aa/ae 357 atomic absorption spectrophotometer. IR data for the compounds were recorded using a Beckman IR 20A spectrophotometer in the frequency range 400–250 cm^{-1}. Samples were prepared as KBr discs. ^1H and ^{13}C NMR spectra of the samples dissolved in DMSO-d_6 were recorded on a Bruker 300 MHz AC-P NMR spectrometer.

Preparation of ligands

N-benzalideneaniline (1a, BENZ), *N*-(2-methoxynaphthalidene)-2-methoxyaniline (2a, 2MeONAP-2MeO), *N*-(2-methoxynaphthalidene)-3-methoxyaniline (3a, 2MeONAP-3MeO) and *N*-(4-methoxynaphthalidene)-2-methoxyaniline (4a, 4MeONAP-2MeO) were synthesized by adding equimolar amounts of the appropriate aniline to aldehyde in 96% ethanol.

Preparation of complex salts

All the complex salts were similarly prepared by reaction of tin(IV) chloride with the appropriate ligand. The preparation of bis[*N*-benzalideneanilinium] hexachlorostannate(IV) $\{[(BENZH)^+]_2[SnCl_6]^{2-}[C_6H_5CHO]\}$ is described as an example.

Tin(IV) chloride pentahydrate (1.05 g, 3 mmol) was added to the ligand (BENZ) (1.09 g, 6 mmol) dissolved in a 1:1 mixed solvent of 96% ethanol and dichloromethane. The mixture was left standing at room temperature for 1 day whereupon light yellowish crystals are obtained. The product was recrystallized from *n*-pentane.

*Crystal structure determination of bis(*N*-benzalideneanilinium) hexachlorostannate(IV) benzaldehyde solvate, $C_{33}H_{30}N_2OCl_6Sn$*

Intensity data for a crystal with dimensions 0.6×0.5×0.18 mm were measured at room temperature on a Huber diffractometer fitted with MoK_α radiation, $\lambda = 0.71069$ Å. The ω scan method was employed to measure a total of 4493 reflections such that $\tau_{max} \geq 27.5°$. No significant decomposition occurred during the data collection. Corrections were applied for Lorentz and polarization effects but not for absorption. There were 2022 unique data of which 1523 satisfied the $F \geq 4\sigma(F)$ criterion of observability and were used in the subsequent analysis. Crystal data are listed in Table 1.

The structure was solved using SHELXS86[9] and refined by a full matrix least squares procedure based on F using SHELX76.[10] All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in their idealized positions (C-H = 0.96 Å) and refined isotropically. A weighting scheme of the form $w = k/[\sigma^2(F_o) + gF_o^2]$ was used, and the refinement continued to final $R = 0.067$, $R_w = 0.070$ for $k = 1$ and $g = 0.0012$. The analysis of variance

Table 1 Crystal data and details of structure refinement for $[(C_6H_5CH{:}NHC_6H_5)^+]_2$ $[SnCl_6]^{2-}$ $[C_6H_5CHO]$.

Formula	$C_{33}H_{30}Cl_6N_2OSn$
Formula weight	802.0
Crystal System	tetragonal
Space group	P4/ncc
a(Å)	13.935(2)
c(Å)	17.996(4)
V(Å^3)	3495(1)
Z	4
D_c(g cm^{-3})	1.323
F(000)	1608
μ (mm^{-1})	1.219
Data collected	4493
Unique Data	2022
R_{int}	0.073
Data with F >4.0 σ(F)	1523
R	0.0666
R_w	0.0703
w	$k/[\sigma^2(F_o)+gF_o^2]$
k	1
g	0.0012
$(\Delta\rho)_{max}$	1.70 (near disordered benzaldehyde molecule)

showed no special features and the maximum residual electron density peak in the final difference map was 1.70 e Å^{-3}. Atomic coordinates are given in Table 2. Bond lengths and angles are listed in Table 3 and the molecular structure together with the atom labelling scheme is shown in Figure 1 which was drawn with ORTEP.[11] The scattering factors of all the atoms were used as incorporated in SHELX76. Tables of anisotropic atomic displacements for non-hydrogen atoms, hydrogen atom

Table 2 Atomic coordinates (x10^4), equivalent isotropic displacement coefficients (Å^2×10^3) and site occupation factors.

	x/a	*y/b*	*z/c*	*U(eq)*	sof
Sn	2500	2500	1976(1)	36(1)	0.25
Cl(1)	2500	2500	3316(2)	46(1)	0.25
Cl(2)	1918(1)	843(1)	1992(1)	51(1)	1
Cl(3)	2500	2500	640(2)	68(1)	0.25
C(1)	532(5)	-857(5)	-2198(3)	46(2)	0.5
N(1)	532(5)	-857(5)	-2198(3)	46(2)	0.5
C(2)	821(5)	-589(5)	-1467(4)	49(2)	1
C(3)	1419(6)	201(5)	-1318(4)	60(3)	1
C(4)	1663(6)	406(6)	-600(5)	70(3)	1
C(5)	1369(6)	-181(6)	-31(5)	67(3)	1
C(6)	783(7)	-965(7)	-166(4)	78(3)	1
C(7)	505(6)	-1167(6)	-872(4)	62(3)	1
C(8)	6883	1857	2107	163(6)	1
C(9)	7500	2500	1721	230(16)	0.5
C(10)	7500	2500	917	416(47)	0.25
O(1)	8025	3047	578	80	0.25

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Bond distances (Å) and angles (°) with e.s.d.'s in parentheses for non-hydrogen atoms.

Sn–Cl(1) 2.412(54)	Cl(1)–Sn–Cl(2) 89.3(13)
Sn–Cl(2) 2.447(54)	Cl(2)–Sn–Cl(3) 90.7(13)
Sn–Cl(3) 2.405(54)	Cl(1)–Sn–Cl(3) 180.0(13)
C(1)–C(2) 1.426(33)	Cl(2)–Sn–Cl(2B) 178.6(13)
C(2)–C(3) 1.407(33)	C(1)–C(2)–C(3) 123.2(14)
C(3)–C(4) 1.367(32)	C(1)–C(2)–C(7) 117.6(14)
C(4)–C(5) 1.373(33)	C(3)–C(2)–C(7) 119.2(14)
C(5)–C(6) 1.386(33)	C(2)–C(3)–C(4) 119.3(15)
C(6)–C(7) 1.358(32)	C(3)–C(4)–C(5) 120.5(15)
C(8)–C(9) 1.423(32)	C(4)–C(5)–C(6) 121.0(15)
C(9)–C(10) 1.446(32)	C(5)–C(6)–C(7) 119.7(15)
C(10)–O(1) 1.220(27)	C(2)–C(7)–C(6) 120.2(15)
C(1) –N(1)* 1.260(31)	C(9)–C(8)–C(8B) 119.2(13)
C(2) –C(7) 1.410(33)	C(8)–C(9)–C(8A) 121.5(13)
H(N1)...Cl(2) 2.834(32)	C(8)–C(9)–C(10) 119.2(13)
	C(9)–C(10)–O(1) 120.0(13)

*N(1) related by the symmetry operation *-y*, *-x*, -0.5-*z*.

coordinates and their corresponding atomic displacement parameters and structure factors are available from the authors.

RESULTS AND DISCUSSION

The reaction of $SnCl_4$ with BENZ results in the formation of a complex salt for which the molecular structure is shown in Figure 1. A packing diagram projected on the crystallographic *ab* plane is depicted in Figure 2. The hexachlorostannate(IV) anion exhibits octahedral geometry and lies between two unipositively charged

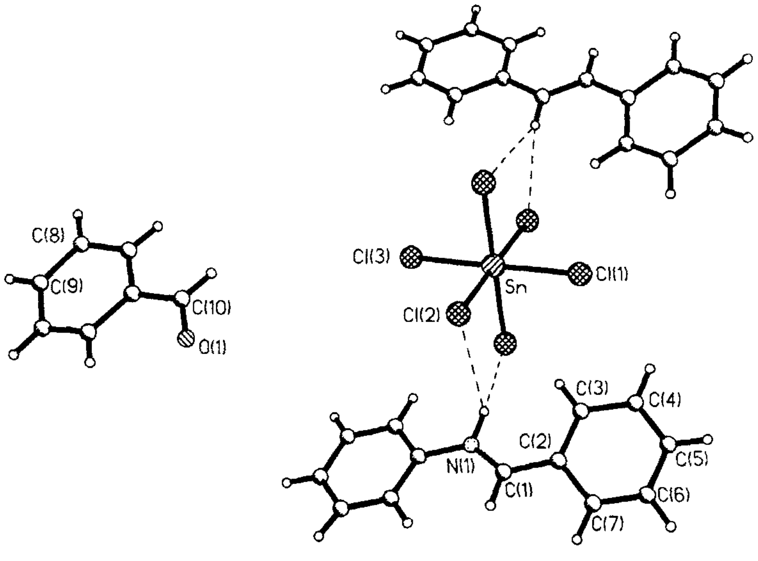


Figure 1 Crystal structure of $[(BENZH)^+]_2[SnCl_6]^{2-}[C_6H_5CHO]$.

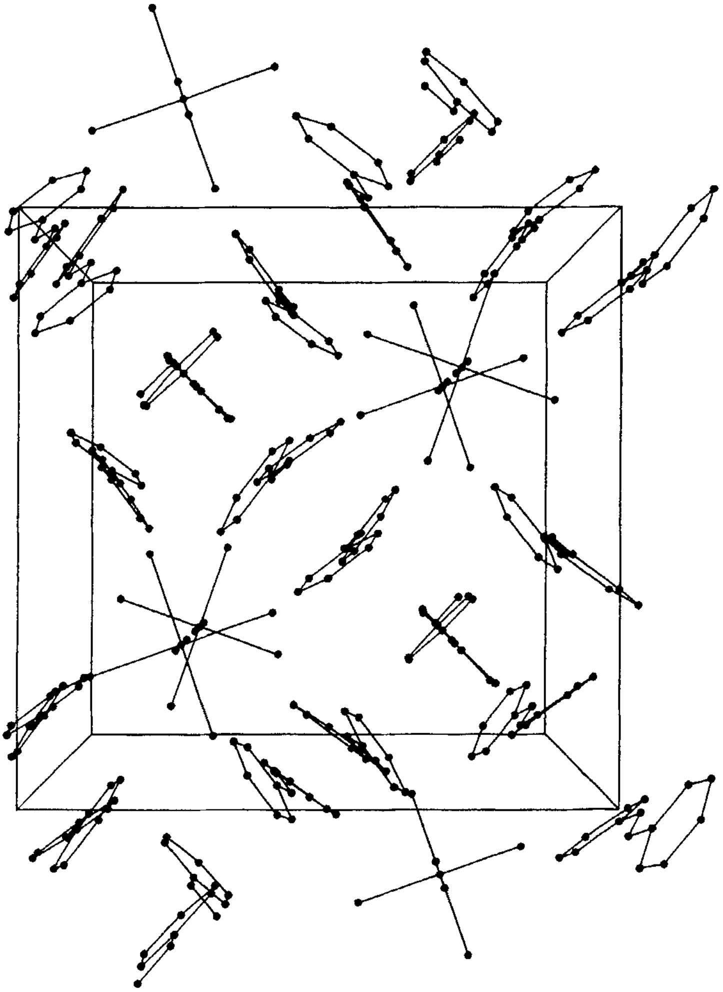


Figure 2 View of unit cell projected on the *ab* plane.

Schiff bases [(BENZH)$^+$]. There is no direct intermolecular contact between the two Schiff base molecular ions as compared to the complex salt resulting from the interaction of triphenyltin isothiocyanate and *N*-(2-hydroxybenzalidene)-2-methoxyaniline in which a proton links the phenolic oxygen atoms of two adjacent ligands.[12] The two positively charged ligands possess *trans* $[PhHC=NHPh]^+$ geometry. The protonation of the imine nitrogen is substantiated by the lengthening of the bond distance C(1)-N(1)*(*symmetry operation: -*y*, -*x*, −05-z; 1.26(3) Å) compared to the corresponding bond distance of neutral benzylidineaniline (1.237(4) Å).[13] Further support is derived from the IR data (Table 5) which shows a new peak at 3255 cm^{-1} not observed in the neutral ligand and the significant shift of the stretching vibration of C = N (from 1624 to 1655 cm^{-1}) upon complex salt

Table 4 Microanalysis results for BENZ, 2MeONAP-2MeO, 2MeONAP-3MeO, 4MeONAP-2MeO and their complexes.

Compound	Formula	Melting point (°)	Calculated(%)	Found(%)
			Sn C H N	Sn C H N
BENZ	$C_{13}H_{11}N$	45–47	86.14 6.13 7.72	86.11 6.07 7.70
2MeONAP-2MeO	$C_{19}H_{17}NO_2$	73–75	78.32 5.89 4.81	78.02 5.77 4.76
2MeONAP-3MeO	$C_{19}H_{17}NO_2$	78–80	78.32 5.89 4.81	78.57 5.71 4.71
4MeONAP-2MeO	$C_{19}H_{17}NO_2$	142–144	78.32 5.89 4.81	78.11 5.80 4.78
$[(\mathrm{BENZH})^+]_2[\mathrm{SnCl_6}]^{2-}[C_6H_5CHO]$	$C_{33}H_{30}N_2OCl_6Sn$	229–231	15.20 48.59 3.72 3.58	15.96 48.49 3.76 3.52
$[(\mathrm{2MeONAPH\text{-}2MeO})^+]_2[\mathrm{SnCl_6}]^{2-}$	$C_{38}H_{36}N_2O_4Cl_6Sn$	187–189	12.96 49.82 3.97 3.06	12.44 49.13 3.82 2.99
$[(\mathrm{2MeONAPH\text{-}3MeO})^+]_2[\mathrm{SnCl_6}]^{2-}$	$C_{38}H_{36}N_2O_4Cl_6Sn$	179–181	12.96 49.82 3.97 3.06	12.65 49.59 3.89 3.06
$[(\mathrm{4MeONAPH\text{-}2MeO})^+]_2[\mathrm{SnCl_6}]^{2-}$	$C_{38}H_{36}N_2O_4Cl_6Sn$	240	12.96 49.82 3.97 3.06	12.28 49.62 3.87 3.17

Table 5 Selected IR data (cm^{-1}) for BENZ, 2MeONAP-2MeO, 2MeONAP-3MeO, 4MeONAP-2MeO and their complexes.

Compound	$\nu_{N\text{-}H}$	$\nu_{CH:N}$
BENZ		1624
2MeONAP-2MeO		1620
2MeONAP-3MeO		1620
4MeONAP-2MeO		1630
$[(BENZH)^+]_2[SnCl_6]^{2-}[C_6H_5CHO]$	3255	1655
$[(2MeONAPH\text{-}2MeO)^+]_2\ [SnCl_6]^{2-}$	3430	1625
$[(2MeONAP\text{-}3MeO)^+]_2[SnCl_6]^{2-}$	3240	1625
$[(4MeONAPH\text{-}2MeO)^+]_2\ [SnCl_6]^{2-}$	3225	1645

formation. Furthermore, ^1H NMR data (Table 6) shows that the peak assignable to the azomethine proton (CH = N) at δ = 8.62 ppm is shifted upfield by 0.2 ppm upon complex salt formation and a new peak at δ = 9.12 ppm which is attributed to the imine nitrogen proton is observed in the spectrum of the complex salt.

$SnCl_4$ has been converted to $[SnCl_6]^{2-}$ which resembles that in the complex salts derived from the reactions of $SnCl_4$ with the respective tetrathiafulvalenium[14] and dibenzotetraselenafulvalenium.[15] The formation of $[SnCl_6]^{2-}$ can be ascribed to the addition to $SnCl_4$ of Cl^- ions present in dichloromethane as has been previously reported.[7,16] While the Sn-Cl(1) and Sn-Cl(3) bond lengths are within the range of 2.40(2)-2.423(3) Å found for Sn-Cl bonds in other salts,[17] the Sn-Cl(2) bond length is comparatively longer (2.45(4) Å). This observation coupled with the fact that the H(N1)...Cl(2) distance is 2.83(3) Å indicates the presence of hydrogen bonding between $[SnCl_6]^{2-}$ and the protonated Schiff bases.[18,19] The Cl(1)-Sn-Cl(2) (89.3(13)°) and Cl(2)-Sn-Cl(3) (90.7(13)°) angles resemble those of a regular octahedron.

One of the interesting features of this complex is that a benzaldehye molecule is present in the crystal lattice in the complex salt $[(BENZH)^+]_2[SnCl_6]^{2-}$ to benzaldehyde (C_6H_5CHO) ratio of 1:1. Microanalytical data for the complex salt (Table 6) agree with the formulation $[(BENZH)^+]_2[SnCl_6]^{2-}[C_6H_5CHO]$. The cocrystallization of benzaldehyde is further substantiated by the appearance of a C = O stretching band at 1704 cm^{-1} in the IR spectrum of the complex. The occurrence of bands attributable to aldehyde C-H stretching at 2820 and 2760 cm^{-1} are within the range of 2880–2650 cm^{-1} reported for aldehydes.[20] The presence of benzaldehyde has also been evidenced by the ^1H NMR wherein a new peak assignable to the benzylic proton ArCHO is observed at δ = 10.04 ppm. A peak due to the benzylic carbon which is absent in the ^{13}C NMR spectrum of the free ligand is found at δ = 193.11 ppm upon reaction with $SnCl_4$.

Microanalytical data for the complex derived from the reaction of $SnCl_4$ with 2MeONAP-2MeO (Table IV) are consistent with the formulation

Table 6 Selected ^1H chemical shifts (ppm) for BENZ, 2MeONAP-2MeO, 2MeONAP-3MeO, and their complexes.

Compound	$^{\delta}C = NH$	$^{\delta}CH = N$
BENZ		8.62
2MeONAP-2MeO		9.49
2MeONAP-3MeO		9.46
$[(BENZ)^+]_2[SnCl_6]^{2-}[C_6H_5CHO]$	9.12	8.42
$[(2MeONAPH\text{-}2MeO)^+]_2[SnCl_6]^{2-}$	10.77	9.12
$[(2MeONAPH\text{-}3MeO)^+]_2[SnCl_6]^{2-}$	10.78	9.15

$[(2MeONAPH\text{-}2MeO)^+]_2[SnCl_6]^{2-}$. A striking feature of its IR spectrum is the appearance of a band at 3430 cm^{-1} ($\nu_{N\text{-}H}$) which is not found in the original ligand 2a, suggesting that protonation of the Schiff base occurs after its reaction with $SnCl_4$. The presence of the N-H peak at δ = 10.77 ppm in the ^1H NMR spectrum of $[(2MeONAPH\text{-}2MeO)^+]_2[SnCl_6]^{2-}$ also supports the existence of the positively charged Schiff base $[(2MeONAPH\text{-}2MeO)^+]$. Analytical data for the complexes resulting from the reactions of $SnCl_4$ with 2MeONAP-3MeO and 4MeONAP-2MeO agree well with the formulations $[(2MeONAPH\text{-}3MeO)^+]_2[SnCl_6]^{2-}$ and $[(4MeONAPH\text{-}2MeO)^+]_2[SnCl_6]^{2-}$, respectively. The respective N-H bands in the IR spectra and the peaks assignable to the N-H proton for complexes $[(2MeONAPH\text{-}3MeO)^+]_2[SnCl_6]^{2-}$ and $[(4MeONAPH\text{-}2MeO)^+]_2[SnCl_6]^{2-}$ are also observed in the same region as for $[(2MeONAPH\text{-}2MeO)^+]_2[SnCl_6]^{2-}$ and their structures are postulated to be similar to that of $[(2MeONAPH\text{-}2MeO)^+]_2[SnCl_6]^{2-}$.

Acknowledgements

The authors (S.G.T., S.B.T.) would like to thank the Malaysian Government and Universiti Sains Malaysia for grant No. 123/3203/2504. J.P.D. thanks the FNRS (Belgium) for financial support.

References

1. B.K. Dwivedi, K. Bhatnagar and A.K. Srivastava, *Synth. React. Inorg. Met. -Org. Chem.*, **16**, 841 (1986).
2. T.N. Srivastava and A.K.S. Chauhan, *Synth. React. Inorg. Met.- Org. Chem.*, **7**, 373 (1977).
3. L.E. Khoo, J.P. Charland, E.J. Gabe and F.E. Smith, *Inorg. Chim. Acta*, **128**, 139 (1987).
4. J.P. Charland, F.L. Lee, E.J. Gabe, L.E. Khoo and F.E. Smith, *Inorg. Chim Acta*, **130**, 55 (1987).
5. H.K. Fun, S.B. Teo, S.B. Teoh and G.Y. Yeap, *Acta Cryst.*, **C47**, 1845 (1991).
6. S.G. Teoh, S.B. Teo, G.Y. Yeap and J.P. Declercq, *Polyhedron*, **10**, 2683 (1991).
7. S.G. Teoh, S.B. Teo, G.Y. Yeap and J.P. Declercq, *Polyhedron*, **11**, 2351 (1992).
8. S.G. Teoh, S.B. Teo, G.Y. Yeap and H.K. Fun, *J. Organomet. Chem.*, **439**, 139 (1992).
9. G.M. Sheldrick, SHELXS86, *A Program for Crystal Structure Determination*, (University of Göttingen, Federal Republic of Germany, 1986).
10. G.M. Sheldrick, SHELX76, *A Program for Crystal Structure Determination and Refinement*, (University of Cambridge, England, 1976).
11. C.K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tenessee, U.S.A.
12. J.P. Charland, E.J. Gabe, L.E. Khoo and F.E. Smith, *Polyhedron*, **8**, 1897 (1989).
13. H.B. Burgi and J.D. Dunitz, *Helv. Chim. Acta*, **53**, 1747 (1970).
14. K. Kondo, G. Matsubayashi and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, 379 (1984).
15. R. Shimizu, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta*, **122**, 37 (1986).
16. R. Jones, C.P. Warrens, D.J. Williams and J.D. Woollins, *J. Chem. Soc., Dalton Trans.*, 907 (1987).
17. J.J. Zubieta and J.J. Zuckerman, *Prog. Inorg. Chem.*, **24**, 251 (197).
18. R.C. Gearhart, T.B. Brill, W.A. Welsh and R.H. Wood, *J. Chem. Soc., Dalton Trans.*, 359 (1973).
19. W. Fuller, *J. Phys. Chem.*, **63**, 1705 (1959).
20. V.M. Parikh, *"Absorption Spectroscopy of Organic Molecules"*, (Addison-Wesley British Columbia, 1974).